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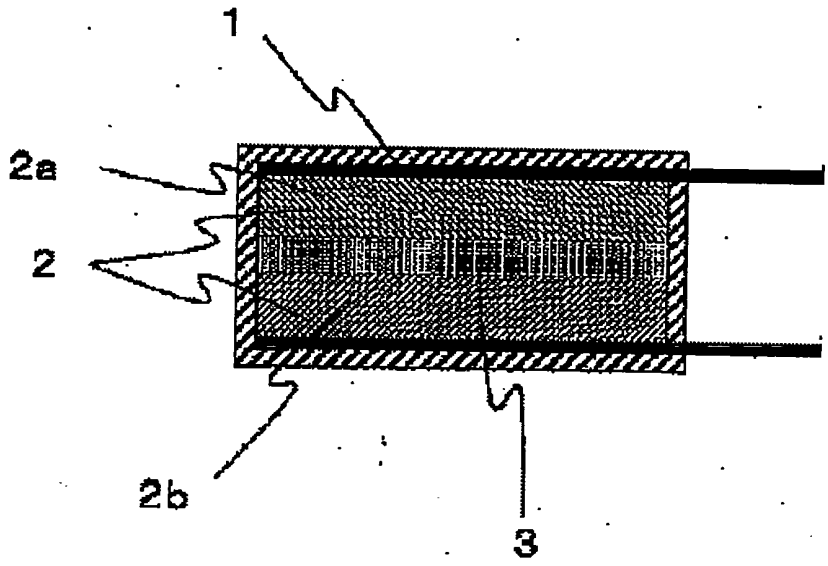
(54) LITHIUM BATTERY

(57) Abstract:

PROBLEM TO BE SOLVED: To solve the problem that poor bonding between an electrode and a solid electrolyte gives larger internal resistance to a battery, resulting in inferior charging/discharging characteristics.

SOLUTION: A lithium battery has a solid electrolyte arranged between a pair of positive and negative electrodes formed of, mainly, active material, wherein there is a compound with acrylic resin coupled siloxane bonds (Si-O) as main skeletons laid between an active material powder and a solid electrolyte powder.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(51)【国際特許分類第7版】

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(57)【要約】
【課題】電極と固体電解質の接合強度が弱くて電池としての内部抵抗が大きくなり、充放電特性が劣るという問題があった。
【解決手段】主として活物質から成る正負一対の電極間に固体電解質を配設したリチウム電池であって、上記活物質粉末および固体電解質粉末の間にアクリル樹脂が結合したシロキサン結合(Si−O)を主骨格とする化合物が介在していることを特徴とする。

【特許請求の範囲】
【請求項1】主として活物質から成る正負一対の電極間に固体電解質を配設したリチウム電池において、前記活物質粉末および固体電解質粉末の間にアクリル樹脂が結合したシロキサン結合(Si−O)を主骨格とする化合物が介在していることを特徴とするリチウム電池。
【請求項2】前記アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に、RuO_2もしくはSb_2O_3をドープしたSnO_2、またはSnO_2をドープしたIn_2O_3から選択される少なくとも一種以上を添加したことを特徴とする請求項1に記載のリチウム電池。
【請求項3】前記アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に炭素材料が結合していることを特徴とする請求項1に記載のリチウム電池

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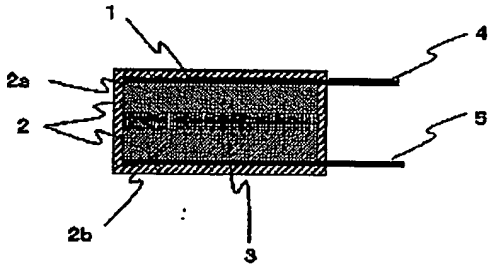
最終頁に続く

(54)【発明の名称】　リチウム電池

(57)【要約】
【課題】　電極と固体電解質の接合強度が弱くて電池としての内部抵抗が大きくなり、充放電特性が劣るという問題があった。
【解決手段】　主として活物質から成る正負一対の電極間に固体電解質を配設したリチウム電池であって、上記活物質粉末および固体電解質粉末の間にアクリル樹脂が結合したシロキサン結合（Si－O）を主骨格とする化合物が介在していることを特徴とする。



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【特許請求の範囲】

【請求項１】 主として活物質から成る正負一対の電極間に固体電解質を配設したリチウム電池において．前記活物質粉末および固体電解質粉末の間にアクリル樹脂が結合したシロキサン結合（Ｓｉ－Ｏ）を主骨格とする化合物が介在していることを特徴とするリチウム電池。

【請求項２】 前記アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に、RuO_2もしくはSb_2O_3をドープしたSnO_2、またはSnO_2をドープしたIn_2O_3から選択される少なくとも一種以上を添加したことを特徴とする請求項１に記載のリチウム電池。

【請求項３】 前記アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に炭素材料が結合していることを特徴とする請求項１に記載のリチウム電池

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明はリチウム電池に関する。

【０００２】

【従来技術】リチウムイオン電池は．高エネルギー密度である特性を活かし、携帯電話やノートパソコン等の電源として広く用いられている。

【０００３】これらリチウムイオン電池は、円筒型と角型があるが、いずれも正極と負極がセパレータを介して捲回された極群を電槽缶内に挿入し．有機電解液を注入して封口された構造となっている。この有機電解液は、プロピレンカーボネート（ＰＣ）、ジメチルエタン（ＤＭＥ）、ジエチルカーボネート（ＤＭＥ）、エチレンカーボネート（ＥＣ）などが単独もしくは混合されたものを溶媒として．これにリチウム塩として$LiClO_4$．$LiPF_6$．$LiBF_4$などが溶解されたものである。

【０００４】近年、ビデオ撮影装置やノートパソコン、携帯電話などの携帯用情報端末機器に代表される各種電子応用機器の薄型かつ軽量小型化の要求に伴い．前述のような有機電解液に代えて．正負一対の電極間に高分子電解質と有機電解液を混合して配設したポリマー電解質電池が注目されている。

【０００５】しかし、これらリチウムイオン電池およびポリマー電池は．有機電解液を含むため、漏液や発煙等の問題を起す可能性がある。

【０００６】かかる問題を解決するために、電解質に無機系の固体電解質を用いたリチウム電池の開発が盛んに行われている。

【０００７】このような無機系の固体電解質を用いたリチウム電池では．硫化物系のガラスから成るリチウムイオン伝導性の無機固体電解質を用いたリチウム電池が上げられる。この無機固体電解質は、有機電解液に匹敵するリチウムイオン伝導度を有している。しかしながら、硫化物系のガラスは、反応性に富み．特に水分や空気と反応し易いという問題がある。

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【０００８】これに対して．酸化物系の固体電解質の中では．ナトリウムイオン伝導性固体電解質（ＮＡＳＩＣＯＮ系材料）と同様の結晶構造を有するリチウムイオン伝導性結晶質固体電解質は．近年では．1×10^{-3}～$1\times10^{-4}S\cdot cm^{-1}$のリチウムイオン伝導率を有する固体電解質が提案されている。

【０００９】例えば、特開平５－２９９１０１号公報では．$Li_{x-(4-n)y}M_yTi_{2-x}(PO_4)_3$（Ｍは１価または２価の陽イオン、Ｍが１価のときｎ＝１、Ｍが２価のときｎ＝２、ｘは０．１～０．５）で表わされる粒状電解質等を焼結させることにより、1×10^{-3}～$1\times10^{-4}S\cdot cm^{-1}$のリチウムイオン伝導率を得ることができている。

【００１０】また、特開平１０－９７８１１号公報では．所定の組成比のP_2O_5．SiO_2、TiO_2．Al_2O_3、Li_2Oなどを溶融して成形した後、熱処理によって$Li_{1+x-y}Al_yTi_{2-y}P_{3-x}O_{12}$（$0\leq x\leq0.4$．$0<y\leq0.6$）を析出させることにより．$1.0\times10^{-3}$～$2.0\times10^{-3}S\cdot cm^{-1}$のリチウムイオン伝導度を有する固体電解質を提案している。

【００１１】また、特開平６－１１１８３１号公報では．MnO_2またはアルカリ金属とマンガンとの複合酸化物からなる正極と固体電解質とが一体形成されてなる固体電解質で．固体電解質がMnO_2またはアルカリ金属とマンガンとの複合酸化物にリチウム化合物を反応させて正極の表面に$LiMnO_2$層を形成することにより．正極と固体電解質との界面の接触面積を大きくして．電池の内部抵抗を小さくし、充放電特性を向上させることを提案している。

【００１２】また、特開平８－１３８７２４号公報では．固体電解質層、もしくは正極活物質粉末と固体電解質粉末の混合物から成る正極と負極活物質粉末と固体電解質粉末の混合物から成る負極とによって固体電解質粉末を加圧成形して得られた固体電解質層を挟持した後、前記固体電解質の軟化点以上でガラス転移点以下の温度で加圧することにより、面接触になって粒界抵抗が小さくなる固体電解質層が得られることを提案している。

【００１３】また、特開平６－７６８２８号公報では、高いイオン伝導性と、機械強度、高い加工性を併せ持ったリチウムイオン導電性固体電解質成形体を得るために．リチウムイオン導電性硫化物固体電解質と高分子弾性体を乾式混練する方法が提案されている。

【００１４】

【発明が解決しようとする課題】従来．固体電解質を用いる電池の場合．電極と固体電解質の接合は、圧接のみで形成される場合が多く．電極と固体電解質の接触面積が小さくて接合強度が弱くなり、これらの界面における抵抗が大きくなって、電池としての内部抵抗が大きくなり．充放電特性が劣るという欠点があった。特に充放電電流が大きくなるに従い．電池の内部抵抗に起因する電

圧降下が大きくなり、電流密度が制限されるという問題があった。

【００１５】また、結晶質の固体電解質は、イオン伝導経路に異方性を有しているものが多いため、固体電解質内の粒界抵抗が問題となる。従って、結晶質の固体電解質は、焼結体を用いることが多く、特開平５－２９９０１号公報のリチウム電池は、この問題を改善する提案となっている。しかしながら、このイオン伝導経路の問題は、電極と固体電解質界面に関しても該当し、圧接のみによる接触では界面の抵抗が大きくなるという問題が残されている。

【００１６】特開平６－１１１８３１号公報のリチウム電池は、電極と固体電解質の界面抵抗を改善する提案であるが、この方法は、MnO_2の形成をスパッタリングで行ったり、Li_2MnO_3の形成を前述のMnO_2とＬｉＯＨとを反応させるなどプロセスが煩雑であるという問題がある。

【００１７】特開平８－１３８７２４号公報のリチウム電池は、固体電解質の軟化点以上でガラス転移点以下の温度で加圧成形するものであるが、この場合、固体電解質内の粒界が低減され、固体電解質としてのリチウムイオン伝導度は向上するものの、加熱処理の工程において、電極と固体電解質の界面に反応層を形成し、その反応層がリチウムイオン伝導を阻害するという問題がある。

【００１８】さらに、これらの固体電解質を用いたリチウム電池は、前述の通り、無機粉末を加圧成形したり、加圧と加熱を同時に行なうなどして形成されている。したがって、得られるリチウム電池は、固く脆いという問題があった。この問題に対して、特開平６－７６８２８号公報のリチウム電池では、リチウムイオン導電性硫化物固体電解質と高分子弾性体とを乾式混練して成形することにより、機械的強度と高い加工性を併せ持ったリチウムイオン導電性固体電解質成形体を得るというものである。ただし、この場合、リチウムイオン導電性固体電解質は、硫化リチウムを含むことに限定されているため、その作製工程においては大気雰囲気中での操作が困難であり、かつ溶剤にプロトン性溶媒を用いた場合、硫化物非晶質固体電解質が溶媒と反応して硫化水素を生じるため、リチウムイオン導電性固体電解質と高分子弾性体との混合は、乾式混練で行なわなければならないという問題があった。

【００１９】本発明は、上述のような従来の問題点に鑑みてなされたものであり、電極と固体電解質の接合強度が弱くて電池としての内部抵抗が大きくなり、充放電特性が劣るという従来の問題点を解消した固体電解質電池を提供することとともに、リチウム電池に可撓性を付与することを目的とする。

【００２０】

【課題を解決するための手段】上記問題を達成するため

に、請求項１に係るリチウム電池では、主として活物質から成る正負一対の電極間に固体電解質を配設したリチウム電池において、前記活物質粉末および固体電解質粉末の間にアクリル樹脂が結合したシロキサン結合（Ｓｉ－Ｏ）を主骨格とする化合物が介在していることを特徴とする。

【００２１】上記リチウム電池では、前記アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に、RuO_2もしくはSb_2O_5をドープしたSnO_2、またはSnO_2をドープしたIn_2O_3から選択される少なくとも一種以上を添加することが望ましい。

【００２２】上記リチウム電池では、前記アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に炭素材料が結合していることが望ましい。

【００２３】

【発明の実施の形態】以下、請求項１に係るリチウム電池の実施形態について説明する。図１は、請求項１に係るリチウム電池の構成例を示す断面図である。図１において、１はパッケージ、２は一対の電極、２ａは正極、２ｂは負極、３は固体電解質層、４は正極集電体、５は負極集電体である。

【００２４】パッケージ１は、気密性を保持できれば材質には限定されず、例えばアルミニウム製ラミネート材、ニッケル、アルミニウムなどの金属、あるいはシュリンクケースなどを用いることができる。

【００２５】正極集電体４または負極集電体５は、正極２ａまたは負極２ｂの集電のために設けられ、例えばアルミニウム（Ａｌ）、ニッケル（Ｎｉ）、銅（Ｃｕ）などの金属箔を用いることができる。

【００２６】電極２（２ａ、２ｂ）の活物質は、例えばリチウムマンガン複合酸化物、二酸化マンガン、リチウムニッケル複合酸化物、リチウムコバルト複合酸化物、リチウムニッケルコバルト複合酸化物、リチウムバナジウム複合酸化物、リチウムチタン複合酸化物、酸化チタン、酸化ニオブ、酸化バナジウム、酸化タングステンなどとそれらの誘導体が挙げられる。さらに固体電解質３を用いたリチウム電池では、セパレータや有機電解液を用いないために、充放電に伴う電極の膨張収縮を許容する制限がある。したがって、電極２（２ａ、２ｂ）に用いる活物質としては、特に$Li_{1-x}Mn_{2-x}O_4$（$0 \leq x \leq 0.2$）、$LiMn_{2-y}Me_yO_4$（Ｍｅ＝Ｎｉ、Ｃｒ、Ｃｕ、Ｚｎ．$0 < y \leq 0.6$）、$Li_4Ti_5O_{12}$、または$Li_4Mn_5O_{12}$のいずれかが選択されることが望ましい。ここで、正極活物質と負極活物質には明確な区別はなく、２種類の化合物の充放電電位を比較して貴な電位を示すものを正極に、卑な電位を示すものを負極にそれぞれ用いて任意の電圧の電池を構成することができる。

【００２７】この活物質粉末の間にアクリル樹脂が結合したシロキサン結合（Ｓｉ－Ｏ）を主骨格とする化合物

を介在させる。シロキサン結合を形成する化合物としては、シラン化合物が上げられる。シラン化合物では、テトラメトキシシラン、メチルトリメトキシシラン、ジメチルジメトキシシラン、フェニルトリメトキシシラン、ジフェニルジメトキシシラン、テトラエトキシシラン、メチルトリエトキシシラン、ジメチルジエトキシシラン、フェニルトリエトキシシラン、ジフェニルジエトキシシラン、ヘキシルトリメトキシシラン、ポリメトキシシロキサン、ポリエトキシシロキサン、ポリブトキシシロキサンなどが挙げられる。これらシラン化合物とアクリル樹脂を結合させる方法としては、アクリル系とシラン系をコールドブレンドし、加水分解させる方法が挙げられる。また、必要に応じてメタノール、エタノール、あるいはイソプロピルアルコール等の溶剤を混合し、加水分解と同時にこれら溶剤を蒸発させることもできる。アクリル樹脂との結合性からするとシラン化合物としては、ポリメトキシシロキサン、ポリエトキシシロキサン、ポリブトキシシロキサンが好ましい。

【0028】電極2と固体電解質3の接合は、圧着や反応層によるものではなく、活物質粉末の間に介在させるアクリル樹脂が結合したシロキサン結合を主骨格とする化合物によって形成する。このアクリル樹脂が結合したシロキサン結合は、熱処理によって形成されるものであると同時に、活物質粉末、固体電解質粉末および電極と固体電解質の結合を形成する。アクリル樹脂が結合したシロキサン結合を形成する場合、過度に温度を上昇させる必要もなく、電極2と固体電解質3の反応を抑えられ、またアクリル樹脂が結合したシロキサン結合を主骨格とする化合物も電極活物質との反応を抑えることができる。

【0029】また、電極活物質の間に介在するアクリル樹脂が結合したシロキサン結合を主骨格とする化合物は、リチウムイオン伝導性結晶化ガラスとも強固な結合を形成し、電極2と固体電解質3の接合を強固にすることができる。したがって、界面の接触面積が大きくなることにより、電池の内部抵抗を低減することができる。

【0030】固体電解質3としては、大別して硫化物系と酸化物系に分類される。硫化物系の固体電解質では室温でのリチウムイオン伝導度は、$1\times10^{-3}S\cdot cm^{-1}$と有機電解液に匹敵する特性を有しているが、吸湿性があるなどの問題がある。したがって、固体電解質3は、酸化物系を用いる方が望ましい。その中で、非晶質系の固体電解質は、リチウムイオン伝導度が室温で$1\times10^{-6}S\cdot cm^{-1}$程度であり、十分に特性を満たすことが難しい。それに対して、結晶質の固体電解質は、リチウムイオン伝導度が室温で$1\times10^{-3}S\cdot cm^{-1}\sim1\times10^{-4}S\cdot cm^{-1}$程度である。したがって、用いる固体電解質3は、結晶質の固体電解質であることがより望ましく、特に、リチウム（Li）、チタン（Ti）、リン（P）および酸素（O）元素を含むリチウムイオン伝導性を有する結晶質の固体電解質であることが望ましく、$Li_{1+x}M_xTi_{2-x}(PO_4)_3$（ここでMはAl、Sc、Y、La）、$Li_{1+x}Ti_{2-x}(PO_4)_3$、$Li_{0.5-3x}R_{0.5+x}TiO_3$（ここでRはLa、Pr、Nd、Sm）、$Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$（ここでMはAl、Ga、$0\leq x\leq0.4$、$0<y\leq0.6$）、$Li_{x+(4-a)y}M_yTi_{2-y}(PO_4)_3$（Mは1価または2価の陽イオン）、などが挙げられる。

【0031】電極2（2a、2b）には、必要に応じて電子伝導助剤が添加される。電子伝導助剤としては、例えば、酸化物としてSnO_2やIn_2O_3、TiO_{2-x}、ZnO、Fe_2O_3、ReO_3、MoO_2、RuO_2、VO、WO_2等が挙げられる。安定した低抵抗率を得るためには、RuO_2もしくはSb_2O_3をドープしたSnO_2、またはSnO_2をドープしたIn_2O_3から選択される少なくとも一種以上を含むことが望ましい。また、電子伝導助剤としての添加量は、酸化物を用いる場合、活物質に対して10～50wt%であることが望ましい。電子伝導助剤がこれらの添加量よりも少ない場合、電子伝導性の付与が十分でなく、これらの添加量よりも多い場合、電子伝導は確保できるものの、電子伝導助剤が電極活物質間に介在し、リチウムイオンの伝導を阻害する可能性があり好ましくない。

【0032】また、アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に炭素材料が結合している場合、上記の電子伝導助剤の添加は必要とせず、アクリル樹脂が結合したシロキサン結合を主骨格とする化合物に結合している炭素材料が電子伝導助剤となる。炭素材料としては、アセチレンブラック、カーボンブラック、ケッチェンブラックなどが挙げられる。また、炭素材料は、アクリル樹脂が結合したシラン化合物のOR基（R：メチル基、エチル基等）と置換することにより結合される。

【0033】電極2（2a、2b）および固体電解質3の作製方法としては以下の方法が挙げられる。正極、負極活物質粉末、固体電解質粉末と、必要であれば、電子伝導助剤粉末をあらかじめ混合してアクリル樹脂が結合したシラン化合物に分散させる。必要に応じて、イソプロピルアルコール等の溶剤を添加し、スラリー化するとともにスラリー粘度を調整する。このとき固体電解質粉末には電子伝導助剤粉末の混合は不要である。

【0034】また、アクリル樹脂が結合したシラン化合物を硬化させるためには硬化用触媒を用いることもできる。この硬化用触媒は、粉末を分散させる前に添加しても、粉末を分散させた後に添加してもよい。

【0035】かくして得られたスラリーは、ドクターブレード法もしくはロールコーター法などにより、正極集電体4もしくは負極集電体5上に塗布した後にアクリル樹脂を結合させたシラン化合物を硬化させる。硬化条件は、硬化用触媒を用いた場合、常温から150℃くらい

が適切であり．硬化温度が高いほど保持時間が短くなるが．硬化温度．時間は特に制限されるものではない。また．硬化用触媒を用いない場合、１５０℃以上の温度で加熱することが望ましく．上限の温度はアクリル樹脂が分解反応を起す３００℃程度である。

【００３６】ここで、電極２には、必要に応じて固体電解質３と同一の組成である固体電解質を混合させてもよい。

【００３７】また、正極２ａ、負極２ｂ、固体電解質３の積層方法は．正極２ａ－固体電解質３－負極２ｂの順に積層した後に一括で加熱硬化させる方法、正極２ａ、負極２ｂを別々に成形、加熱硬化した後にいずれか一方の電極上に固体電解質３を成形した後にもう一方の電極を重ねた後に硬化させる方法などが挙げられる。さらに．加熱硬化時に加圧を行なうと紛体の充填率が向上するとともに、電極２－固体電解質３の接合がより強固になるため望ましい。

【００３８】本発明が適用される固体電解質電池は、一次電池であっても二次電池であってもよい。電池形状は円筒型、角型．ボタン型．コイン型および扁平型などに限定されるものではない。

【００３９】

【実施例】［実施例１］水酸化リチウムと二酸化マンガンをＬｉとＭｎのモル比が１．１：１．９となるように混合し、この混合物を大気中の６５０℃で１５時間加熱焼成することによってリチウムマンガン複合酸化物（$Li_{1.1}Mn_{1.9}O_4$）を合成し、これを正極活物質とした。次に水酸化リチウムと二酸化マンガンをＬｉとＭｎのモル比が４：５となるように混合し．この混合物を大気中の６００℃で１５時間加熱焼成することでリチウムマンガン複合酸化物（$Li_4Mn_5O_{12}$）を合成し．これを負極活物質とした。

【００４０】アクリル樹脂が結合したシロキサン化合物は．以下の手順で準備した。アクリル樹脂が結合したシロキサン化合物（シロキサン化合物濃度：約３０ｗｔ％．アクリル樹脂濃度：約２０ｗｔ％．溶剤：約５０ｗｔ％）に対し．マレイン酸系の硬化用触媒を混合し、常温にて撹拌して混合液を作製した。この時、硬化用触媒の混合比は、アクリル樹脂が結合したシロキサン化合物１００ｇに対して３ｇとした。また．混合液の安定化を図るために、常温にて１２時間静置した。（以下これを調整混合液とする。）

前述の正極および負極活物質を電子伝導助剤であるRuO_2と共に調整混合液にそれぞれ分散させてスラリーを作製した。このときの活物質粉末、RuO_2．調整混合液の混合比は重量比で２：１：１とした。次いで．このスラリーをドクターブレード法でアルミ箔上に成形した後に．１５０℃３０分の条件で加熱硬化させた。さらに．これを２５ｍｍ×２５ｍｍのサイズに裁断し正極２ａ負極２ｂを得た。このときの厚みは正極２ａおよび負極２ｂとも７５μｍであった。

【００４１】固体電解質３としては．主結晶相が$Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$で表わせられる結晶質の固体電解質を用いた。粉末状の固体電解質を調整混合液に分散させてスラリーを作製した。このスラリーを前述の正極２ａ上にドクターブレード法で成形し．次いで負極２ｂを塗布した固体電解質３上に重ね合わせ１５０℃３０分の条件で加熱硬化させ、正極２ａ－固体電解質３－負極２ｂの積層体を作製した。このときの固体電解質３の厚みは３０μｍであった。

【００４２】得られた積層体をパッケージ１のアルミ製ラミネートに装着した。アルミ製ラミネートは３５ｍｍ×３５ｍｍのサイズに切断したものを２枚準備し．集電体を接合した積層体を挟んでアルミ製ラミネートの外周部を熱圧着することで、図１に示した３５ｍｍ×３５ｍｍの角型リチウム電池を組み立てた。

【００４３】［実施例２］正極活物質および負極活物質の合成方法は実施例１と同様に行なった。

【００４４】アクリル樹脂が結合したシロキサン化合物には．炭素材料が結合したもの（シロキサン化合物濃度：約２５ｗｔ％、アクリル樹脂濃度：約１５ｗｔ％、アセチレンブラック濃度：約１０ｗｔ％、溶剤：約５０ｗｔ％）を用いた。

【００４５】以下、調整混合液の作製．正極２ａ－固体電解質３－負極２ｂの作製方法は、実施例１と同様に行なった。ここで得られた電極の厚みは７０μｍであり、固体電解質の厚みは３５μｍであった。

【００４６】角型リチウム電池の作製方法は実施例１と同様に行なった。

【００４７】［比較例１］正極活物質および負極活物質の合成方法は実施例１と同様に行なった。

【００４８】電極の形成は以下の手順で行った。先に得られた正極および負極活物質とカーボンブラックをポリフッ化ビニリデンを溶解させたＮ－メチル－２－ピロリドンに各々分散させてスラリーを調整した。このとき、電極活物質、カーボンブラックおよびポリフッ化ビニリデンの混合比は重量比で８５：１２：７とした。

【００４９】得られたスラリーをドクターブレード法でアルミ箔上に塗付して、Ｎ－メチル－２－ピロリドンを除去することで正極および負極の電極を得た。得られた電極活物質の粉体充填率を更に向上させる目的でロール加圧し、さらに得られた電極シートを２５ｍｍ×２５ｍｍのサイズに裁断して電極を得た。得られた電極の厚みは各々７０μｍであった。

【００５０】固体電解質は．電極と同様に、ポリフッ化ビニリデンを溶解させたＮ－メチル－２－ピロリドンに分散させてスラリーを調整した。このとき、固体電解質とポリフッ化ビニリデンの混合比は重量比で９３：７とした。

【００５１】得られたスラリーを先に得られた正極上に

塗付して、Ｎ－メチル－２－ピロリドンを除去することで正極－固体電解質の積層体を得た。さらに、この積層体の固体電解質側に、先に得られた負極を重ね、密着性を向上させる目的で、１６０℃の温度で加圧した。このときの加圧荷重は８０ＭＰａとした。また、固体電解質の厚みは２７μｍであった。

【００５２】得られた積層体を用いて実施例１と同様にして角型のリチウム電池を組み立てた。

【００５３】〔比較例２〕正極活物質および負極活物質の合成方法は、実施例と同様に、電極の形成は、比較例１と同様に行なった。このときの電極厚みは、各々６５μｍであった。

【００５４】固体電解質は、$Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$で表わせられる結晶質の厚み５０μｍのバルク体を用いた。この固体電解質バルク体を先に得られた電極で挟持し、正極－固体電解質－負極の積層体を作製した。

＊【００５５】得られた積層体を用いて実施例１と同様にして角型のリチウム電池を組み立てた。

【００５６】（評価）かくして得られた角型固体電解質電池を用いて、充放電装置により、充電条件として１００μＡ／ｃｍ²、２００μＡ／ｃｍ²、５００μＡ／ｃｍ²の電流で前述の角型固体電解質電池に１．５Ｖまで充電を行い、電圧が１．５Ｖに到達した後、充電を停止して５分間保持し、その後０．５Ｖの電圧まで充電時と同じ電流で放電し、次に再度１．５Ｖまで充電し、この電圧に到達した後、充電を停止して５分間保持する充放電サイクル評価を行った。

【００５７】その結果を表１に示す。なお、表中の数字は各放電電流に対する放電容量を示し、単位はｍＡｈである。

【００５８】

【表１】

	放電電流 〔μＡ／ｃｍ²〕		
	１００	２００	５００
実施例１	１８．５	１７．８	１７．１
実施例２	１８．３	１７．５	１６８
比較例１	６．６	４．３	－
比較例２	１６．２	１５．３	１４．４

【００５９】また、実施例１、実施例２、比較例１、および比較例２で作製した正極－固体電解質－負極の積層体を用いて可撓性の評価を行なった。評価方法は、直径１０ｍｍの円柱状のガラス棒に巻き付け積層体の割れおよびクラックを確認した。その結果、固体電解質にバルク体を用いた比較例２以外は割れおよびクラックは、確認されなかった。

【００６０】以上のことから、本発明のリチウム電池は、固体電解質バルク体を用いたリチウム電池と同等の充放電特性が得られるとともに、可撓性にも優れていることがわかる。特に放電電流が大きくなっても放電電流の低下が小さいことが顕著である。

【００６１】これは、正極および負極活物質の間にシロキサン結合を主骨格とする化合物を介在させることにより、電極と固体電解質の接合を可能とし、さらに界面の抵抗が低減されたためと考えられる。さらに、本発明に寄れば、熱処理の過程においてシロキサン結合を形成するため、電極活物質との反応が起こりにくく、電極活物質本来の特性を保ちつつ電極活物質粉末の接合および電極と固体電解質の接合を行なっていると考えられる。また、シロキサン結合を主骨格とする化合物には、アクリル樹脂が結合されているために可撓性も備えることが可能となる。

【００６２】

【発明の効果】以上のように、本発明に係わる固体電解質電池によれば、電極を構成する活物質粉末および固体電解質粉末の間に、アクリル樹脂が結合したシロキサン結合（Ｓｉ－Ｏ）を主骨格とする化合物を介在させることにより、電極と固体電解質の接合が強固になる。もって界面の接触面積が大きくなって電池の内部抵抗を低減することができ、充放電特性に優れたリチウム電池を得ることができる。

【００６３】さらに、シロキサン結合にアクリル樹脂が結合していることから、可撓性を備えることが可能となり、フレキシビリティー性に優れるリチウム電池を得ることができる。

【００６４】

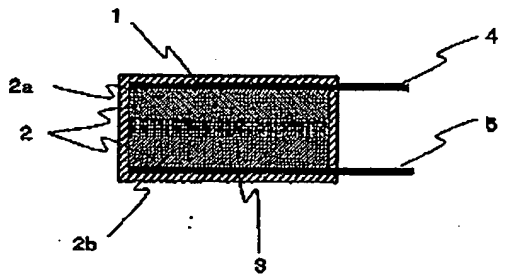
【図面の簡単な説明】

【図１】本発明に係わるリチウム電池の一実施形態を示す断面図である。

【符号の説明】

１：パッケージ、２：一対の電極、２ａ：正極、２ｂ：負極、３：固体電解質層、４：正極集電体、５：負極集電体

【図1】



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* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The lithium cell characterized by the compound which makes the main skeleton siloxane combination (Si-O) which acrylic resin combined between the aforementioned active material powder and solid electrolyte powder in the lithium cell which arranged the solid electrolyte in inter-electrode [of the positive/negative couple which consists mainly of an active material] intervening.

[Claim 2] The lithium cell according to claim 1 characterized by the thing which is chosen as the compound which makes the main skeleton siloxane combination which the aforementioned acrylic resin combined from In 2O3 which doped SnO2 or SnO2 which doped RuO2 or Sb 2O3, and which added more than a kind at least.

[Claim 3] The lithium cell according to claim 1 characterized by the carbon material having combined with the compound which makes the main skeleton siloxane combination which the aforementioned acrylic resin combined.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to a lithium cell.
[0002]
[Description of the Prior Art] The lithium ion battery is widely used as power supplies, such as a cellular phone and a notebook computer, taking advantage of the property which is high-energy density.
[0003] Although these lithium ion batteries have cylindrical and a square shape, all insert the electrode group by which the positive electrode and the negative electrode were ****(ed) through separator into a battery-case can, and they have structure which it obturated by pouring in the organic electrolytic solution. LiClO4, LiPF6, LiBF4, etc. are dissolved in this as lithium salt by using that this organic electrolytic solution has propylene carbonate (PC), dimethyl ethane (DME), diethyl carbonate (DME), independent ethylene carbonate (EC), etc. or the mixed thing as a solvent.
[0004] In recent years, with the thin shape of the various electronic application devices represented by portable information terminal equipments, such as video photography equipment, and a notebook computer, a cellular phone, and the demand of a lightweight miniaturization, it replaces with the above organic electrolytic solutions, and the polymer electrolyte cell which mixed and arranged a polyelectrolyte and the organic electrolytic solution in inter-electrode [of a positive/negative couple] attracts attention.
[0005] However, since these lithium ion batteries and a polymer battery contain the organic electrolytic solution, they may start problems, such as a liquid spill and emitting smoke.
[0006] In order to solve this problem, development of the lithium cell which used the solid electrolyte of an inorganic system for the electrolyte is performed briskly.
[0007] The lithium cell using the inorganic solid electrolyte of lithium ion conductivity which consists of the glass of a sulfide system is raised in the lithium cell using the solid electrolyte of such an inorganic system. This inorganic solid electrolyte has the lithium ion conductivity which is equal to the organic electrolytic solution. However, the glass of a sulfide system is rich in reactivity, and has the problem of being easy to react especially with moisture and air.
[0008] On the other hand, in the solid electrolyte of an oxide system, the solid electrolyte in which a sodium ion conductivity solid electrolyte (NASICON system material) and the lithium ion conductivity crystalline-substance solid electrolyte which has the same crystal structure have the lithium ion conductivity of 1x10-3 - 1x10-4 S-cm -1 in recent years is proposed.
[0009] For example, in JP,5-299101,A, the lithium ion conductivity of 1x10-3 - 1x10-4 S-cm -1 has been obtained by making the granular electrolyte expressed with Li1+(4-n) xMxTi2-x(PO4)3 (2 n= when a univalent or divalent cation and M of M are univalent and n= 1 and M are divalent x 0.1-0.5) sinter.
[0010] Moreover, after fusing and fabricating P2O5 of a predetermined composition ratio, SiO2, TiO2 and aluminum 2O3, Li2O, etc. in JP,10-97811,A, By depositing Li1+x+yAlxTi2-yP3-yO12 (0<=x<=0.4, 0< y<=0.6) with heat treatment, the solid electrolyte which has the lithium ion conductivity of 1.0x10-3 - 2.0x10-3 S-cm -1 is proposed.
[0011] Moreover, in JP,6-111831,A, when a solid electrolyte makes a lithium compound react to the multiple oxide of MnO2 or alkali metal, and manganese and forms three layer of Li2MnO(s) on the

surface of a positive electrode by the solid electrolyte in which it really comes to form the positive electrode which consists of a multiple oxide of MnO2 or alkali metal, and manganese, and a solid electrolyte, the touch area of the interface of a positive electrode and a solid electrolyte was enlarged, internal resistance of a cell was made small, and it has proposed raising a charge-and-discharge property.

[0012] Moreover, after pinching the solid electrolyte layer obtained by carrying out pressing of the solid electrolyte powder in JP,8-138724,A by the solid electrolyte layer or the negative electrode which consists of the mixture of the positive electrode and negative-electrode active material powder which consist of the mixture of positive-active-material powder and solid electrolyte powder, and solid electrolyte powder, it has proposed that the solid electrolyte layer to which it becomes field contact and grain-boundary resistance becomes small is obtained by pressurizing at the temperature below a glass transition point above the softening temperature of the aforementioned solid electrolyte.

[0013] Moreover, in JP,6-76828,A, in order to obtain the lithium ion conductivity solid electrolyte Plastic solid having high ion conductivity, and mechanical strength and high processability, the method of carrying out dry type kneading of a lithium ion conductivity sulfide solid electrolyte and the macromolecule elastic body is proposed.

[0014]

[Problem(s) to be Solved by the Invention] Conventionally, in the case of the cell using a solid electrolyte, it was formed in many cases only with the pressure welding, and the touch area of an electrode and a solid electrolyte was small, the bonding strength became weak, the resistance in these interfaces became large, the internal resistance as a cell became large, and junction of an electrode and a solid electrolyte had the fault that a charge-and-discharge property was inferior. The voltage drop resulting from the internal resistance of a cell became large, and there was a problem that current density was restricted as especially the charge and discharge current became large.

[0015] Moreover, since an ionic conduction path has many which have the anisotropy as for the solid electrolyte of a crystalline substance, the grain-boundary resistance in a solid electrolyte poses a problem. Therefore, the solid electrolyte of a crystalline substance serves as a proposal for which the lithium cell of JP,5-299101,A improves this problem, using a sintered compact in many cases. However, the problem of this ionic conduction path corresponds also about an electrode and a solid electrolyte interface, and the problem that resistance of an interface becomes large is left behind in contact only by the pressure welding.

[0016] Although the lithium cell of JP,6-111831,A is a proposal which improves the interfacial resistance of an electrode and a solid electrolyte, it has the problem that this method has complicated processes, such as forming MnO2 by sputtering or making above-mentioned MnO2 and above-mentioned LiOH formation of Li2MnO3 react etc.

[0017] Although pressing of the lithium cell of JP,8-138724,A is carried out at the temperature below a glass transition point above the softening temperature of a solid electrolyte, the grain boundary in a solid electrolyte is reduced in this case, and although the lithium ion conductivity as a solid electrolyte improves, in the process of heat-treatment, it forms a reaction layer in the interface of an electrode and a solid electrolyte, and has the problem that the reaction layer checks lithium ion conduction.

[0018] Furthermore, as above-mentioned, the lithium cell using these solid electrolytes carries out pressing of the inorganic powder, or performs pressurization and heating simultaneously and is formed. Therefore, the lithium cell obtained had the problem that it was hard and was weak. The lithium ion conductivity solid electrolyte Plastic solid having a mechanical strength and high processability is obtained by carrying out dry type kneading and fabricating a lithium ion conductivity sulfide solid electrolyte and a macromolecule elastic body with the lithium cell of JP,6-76828,A to this problem. However, since a sulfide noncrystalline-solid electrolyte reacted with a solvent and a hydrogen sulfide was produced when operation in air atmosphere is difficult and a protic solvent is used [in / the production process / since it is limited to a lithium ion conductivity solid electrolyte containing a sulfuration lithium in this case] for a solvent, there was a problem that mixture with a lithium ion conductivity solid electrolyte and a macromolecule elastic body had to be performed by

dry type kneading.

[0019] It is made in view of the above conventional troubles, and the bonding strength of an electrode and a solid electrolyte is weak, the internal resistance as a cell becomes large, and this invention aims to let it give flexibility to a lithium cell to offer the solid electrolyte cell which canceled the conventional trouble that a charge-and-discharge property was inferior.

[0020]

[Means for Solving the Problem] In order to attain the above-mentioned problem, in the lithium cell concerning a claim 1, it is characterized by the compound which makes the main frame siloxane combination (Si-O) which acrylic resin combined between the aforementioned active material powder and solid electrolyte powder intervening in the lithium cell which arranged the solid electrolyte in inter-electrode [of the positive/negative couple which consists mainly of an active material].

[0021] The thing which is chosen as the compound which makes the main frame siloxane combination which the aforementioned acrylic resin combined in the above-mentioned lithium cell from In 2O3 which doped SnO2 or SnO2 which doped RuO2 or Sb 2O3 and which add more than a kind at least is desirable.

[0022] It is desirable for the carbon material to have combined with the compound which makes the main frame siloxane combination which the aforementioned acrylic resin combined in the above-mentioned lithium cell.

[0023]

[Embodiments of the Invention] Hereafter, the operation form of the lithium cell concerning a claim 1 is explained. Drawing 1 is the cross section showing the example of composition of the lithium cell concerning a claim 1. drawing 1 -- setting -- 1 -- for a positive electrode and 2b, as for a solid electrolyte layer and 4, a negative electrode and 3 are [a package and 2 / the electrode of a couple, and 2a / a positive-electrode charge collector and 5] negative-electrode charge collectors

[0024] If airtightness can be held, a package 1 is not limited to the quality of the material, for example, can use metals, such as lamination material made from aluminum, nickel, and aluminum, or a shrink case.

[0025] The positive-electrode charge collector 4 or the negative-electrode charge collector 5 is formed for current collection of positive-electrode 2a or negative-electrode 2b, for example, metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), can be used for it.

[0026] As for the active material of an electrode 2 (2a, 2b), for example, a lithium manganese multiple oxide, manganese dioxide, a lithium nickel multiple oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, a niobium oxide, a vanadium oxide, tungstic oxides, etc. and those ****** are mentioned. Furthermore, in the lithium cell using the solid electrolyte 3, in order to use neither separator nor the organic electrolytic solution, there is a limit which permits expansion contraction of the electrode accompanying charge and discharge. Therefore, especially as an active material used for an electrode 2 (2a, 2b), it is desirable to choose either Li1+xMn2-xO4 (0<=x<=0.2), LiMn2-yMeyO4 (Me=nickel, Zn [Cr, Cu and Zn], 0< y<=0.6), Li4Ti 5O12 or Li4Mn 5O12. Here, what shows **** potential to a positive electrode for what a clear distinction does not have in a positive active material and a negative-electrode active material, compares the charge and discharge potential of two kinds of compounds, and shows electropositive potential can be used for a negative electrode, respectively, and the cell of arbitrary voltage can be constituted.

[0027] The compound which makes the main skeleton siloxane combination (Si-O) which acrylic resin combined is made to intervene between this active material powder. A silane compound is raised as a compound which forms siloxane combination. With a silane compound, a tetramethoxy silane, methyl trimetoxysilane, dimethyl dimethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, a tetrapod ethoxy silane, methyl triethoxysilane, dimethyl diethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, hexyl trimethoxysilane, the poly methoxy siloxane, a poly ethoxy siloxane, a poly butoxy siloxane, etc. are mentioned. As a method of combining these silanes compound and acrylic resin, the cold blend of acrylic and the silane system is carried out, and the method of making it understand an added water part is mentioned. Moreover, solvents, such as a methanol, ethanol, or isopropyl alcohol, can be mixed if needed, and these solvents can also be

evaporated simultaneously with hydrolysis. Considering unity with acrylic resin, as a silane compound, the poly methoxy siloxane, a poly ethoxy siloxane, and a poly butoxy siloxane are desirable.

[0028] Junction of an electrode 2 and a solid electrolyte 3 is based neither on sticking by pressure nor a reaction layer, and is formed with the compound which makes the main skeleton siloxane combination which the acrylic resin made to intervene between active material powder combined. Siloxane combination which this acrylic resin combined forms combination of active material powder, solid electrolyte powder and an electrode, and a solid electrolyte at the same time it is formed by heat treatment. When forming siloxane combination which acrylic resin combined, the compound which makes the main skeleton siloxane combination which temperature did not need to be raised too much, and could suppress the reaction of an electrode 2 and a solid electrolyte 3, and acrylic resin combined can also suppress a reaction with an electrode active material.

[0029] Moreover, lithium ion conductivity glass ceramics can form a firm combination, and the compound which makes the main skeleton siloxane combination which the acrylic resin which intervenes between electrode active materials combined can strengthen junction of an electrode 2 and a solid electrolyte 3 for them. Therefore, the touch area of an interface can reduce the internal resistance of a cell by the bird clapper greatly.

[0030] As a solid electrolyte 3, it divides roughly and is classified into a sulfide system and an oxide system. In the solid electrolyte of a sulfide system, although the lithium ion conductivity in a room temperature has the property which is equal to 1x10-3 S-cm -1 and the organic electrolytic solution, it has problems, such as being hygroscopic. Therefore, it is more desirable to use an oxide system for a solid electrolyte 3. In it, lithium ion conductivity is about -one 1x10-6 S-cm at a room temperature, and it is difficult for the solid electrolyte of an amorphous system to fully fulfill a property. The lithium ion conductivity of the solid electrolyte of a crystalline substance is about -one 1x10-3 S-cm - 1 - 1x10-4 S-cm at a room temperature to it. Therefore, as for the solid electrolyte 3 to be used, it is more desirable that it is the solid electrolyte of a crystalline substance. It is desirable that it is the solid electrolyte of the crystalline substance which has the lithium ion conductivity which contains a lithium (Li), titanium (Ti), and a Lynn (P) and oxygen (O) element especially. Li1+xMxTi2-x(PO4)3 (here -- M -- aluminum, Sc, and Y --) La), Li1+xTi2-x(PO4)3, Li0.5-3xR0.5+xTiO3 (it La(s) R here) Pr, Nd, Sm, Li1+x+yMxTi2-xSiyP3-yO12 (M is aluminum, Ga, 0<=x<=0.4, and 0< y<=0.6 here), Li1+(4-n) MxTi2-x(PO4)3 (M is a univalent or divalent cation), etc. are mentioned.

[0031] An electronic-conduction assistant is added by the electrode 2 (2a, 2b) if needed. As an electronic-conduction assistant, SnO2, In 2O3, TiO2-x, ZnO and Fe 3O4, ReO3, MoO2, RuO2 and VO, and WO2 grade are mentioned as an oxide, for example. In order to obtain the stable low resistivity, the thing which is chosen from In 2O3 which doped SnO2 or SnO2 which doped RuO2 or Sb 2O3 and which contain more than a kind at least is desirable. Moreover, when using an oxide, as for the addition as an electronic-conduction assistant, it is desirable that it is 10 - 50wt% to an active material. When there are few electronic-conduction assistants than these additions, grant of electronic-conduction nature is not enough, and when [than these additions] more, although an electronic conduction is securable, an electronic-conduction assistant may intervene between electrode active materials, may check conduction of a lithium ion, and is not desirable [an electronic conduction].

[0032] Moreover, when the carbon material has combined with the compound which makes the main skeleton siloxane combination which acrylic resin combined, addition of the above-mentioned electronic-conduction assistant is not needed, but the carbon material combined with the compound which makes the main skeleton siloxane combination which acrylic resin combined serves as an electronic-conduction assistant. As a carbon material, acetylene black, carbon black, KETCHIEN black, etc. are mentioned. Moreover, a carbon material is combined by replacing by OR machines (R : a methyl group, an ethyl group, etc.) of the silane compound which acrylic resin combined.

[0033] The following methods are mentioned as the production method of an electrode 2 (2a, 2b) and a solid electrolyte 3. The silane compound which mixed electronic-conduction assistant powder beforehand and acrylic resin combined with a positive electrode, negative-electrode active material powder, and solid electrolyte powder when required is distributed. Slurry viscosity is adjusted while

adding and slurring solvents, such as isopropyl alcohol, if needed. At this time, mixture of electronic-conduction assistant powder is unnecessary to solid electrolyte powder.

[0034] Moreover, in order to stiffen the silane compound which acrylic resin combined, the catalyst for hardening can also be used. Before distributing powder, even if it adds, after distributing powder, you may add this catalyst for hardening.

[0035] By the doctor blade method or the roll-coater method, after applying the slurry obtained in this way on the positive-electrode charge collector 4 or the negative-electrode charge collector 5, it stiffens the silane compound which combined acrylic resin. When the catalyst for hardening is used for hardening conditions, although the holding time becomes short so that about 150 degrees C is suitable from ordinary temperature and a curing temperature is high, a curing temperature and especially time are not restricted. Moreover, when not using the catalyst for hardening, it is desirable to heat at the temperature of 150 degrees C or more, and maximum temperature is about 300 degrees C from which acrylic resin starts a decomposition reaction.

[0036] You may make an electrode 2 mix the solid electrolyte which is the same composition as a solid electrolyte 3 here if needed.

[0037] Moreover, the method of stiffening, after having fabricated the method of carrying out heat hardening by package after carrying out the laminating of positive-electrode 2a, negative-electrode 2b, and the laminating method of a solid electrolyte 3 to the order of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b, positive-electrode 2a, and negative-electrode 2b after carrying out heat hardening, fabrication and, fabricating a solid electrolyte 3 on one of electrodes separately and piling up another electrode etc. is mentioned. Furthermore, if it pressurizes at the time of heat hardening, while the filling factor of **** will improve, since junction of the electrode 2-solid electrolyte 3 becomes firmer, it is desirable.

[0038] Even if the solid electrolyte cell to which this invention is applied is a primary cell, it may be a rechargeable battery. A cell configuration is not limited to cylindrical, a square shape, a button type, a coin type, a flat type, etc.

[0039]

[Example] A [example 1] lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 1.1:1.9, by carrying out heating baking of this mixture at 650 degrees C in the atmosphere for 15 hours, the lithium manganese multiple oxide (Li1.1Mn 1.9O4) was compounded, and this was made into the positive active material. Next, a lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 4:5, the lithium manganese multiple oxide (Li4Mn 5O12) was compounded by carrying out heating baking of this mixture at 600 degrees C in the atmosphere for 15 hours, and this was made into the negative-electrode active material.

[0040] The siloxane compound which acrylic resin combined was prepared in the following procedures. To the siloxane compound (siloxane compound concentration : about 30 wt(s)% and acrylic resin concentration : about 20 wt(s)%, a solvent : about 50 wt(s)%) which acrylic resin combined, the catalyst for hardening of a maleic-acid system was mixed, it stirred in ordinary temperature, and mixed liquor was produced. At this time, the mixing ratio of the catalyst for hardening was set to 3g to 100g of siloxane compounds which acrylic resin combined. Moreover, in order to attain stabilization of mixed liquor, it put in ordinary temperature for 12 hours. (Let this be adjustment mixed liquor below.)

Adjustment mixed liquor was made to distribute an above-mentioned positive electrode and an above-mentioned negative-electrode active material with RuO2 which is an electronic-conduction assistant, respectively, and the slurry was produced. The mixing ratio of the active material powder at this time, RuO2, and adjustment mixed liquor was set to 2:1:1 by the weight ratio. Subsequently, after fabricating this slurry by the doctor blade method on aluminum foil, heat hardening was carried out on 150-degree-C conditions for 30 minutes. Furthermore, this was judged in 25mmx25mm size, and positive-electrode 2a negative-electrode 2b was obtained. Positive-electrode 2a and negative-electrode 2b of the thickness at this time were 75 micrometers.

[0041] As a solid electrolyte 3, the main crystal phase used the solid electrolyte of the crystalline substance which can be expressed with Li1+x+yAlxTi2-xSiyP3-yO12. Adjustment mixed liquor was

made to distribute a powdered solid electrolyte, and the slurry was produced. This slurry was fabricated by the doctor blade method on the above-mentioned positive-electrode 2a, it piled up on the solid electrolyte 3 which subsequently applied negative-electrode 2b, heat hardening was carried out on 150-degree-C conditions for 30 minutes, and the layered product of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was produced. The thickness of the solid electrolyte 3 at this time was 30 micrometers.

[0042] The lamination made from aluminum of a package 1 was equipped with the obtained layered product. The lamination made from aluminum prepared two things cut in 35mmx35mm size, is carrying out thermocompression bonding of the periphery section of the lamination made from aluminum on both sides of the layered product which joined the charge collector, and assembled the 35mmx35mm square shape lithium cell shown in drawing 1 .

[0043] The synthetic method of a [example 2] positive active material and a negative-electrode active material was performed like the example 1.

[0044] What the carbon material combined (siloxane compound concentration : about 25 wt(s)% and acrylic resin concentration : about 15 wt(s)% and acetylene black concentration : about 10 wt(s)%, a solvent : about 50 wt(s)%) was used for the siloxane compound which acrylic resin combined.

[0045] Hereafter, the production method of production of adjustment mixed liquor and positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was performed like the example 1. The thickness of the electrode obtained here was 70 micrometers, and the thickness of a solid electrolyte was 35 micrometers.

[0046] The production method of a square shape lithium cell was performed like the example 1.

[0047] The synthetic method of the [example 1 of comparison] positive active material and a negative-electrode active material was performed like the example 1.

[0048] The following procedures performed formation of an electrode. The N-methyl-2-pyrrolidone in which the polyvinylidene fluoride was dissolved was made to distribute respectively the positive electrode and negative-electrode active material which were obtained previously, and carbon black, and the slurry was adjusted. At this time, the mixing ratio of an electrode active material, carbon black, and a polyvinylidene fluoride was set to 85:12:7 by the weight ratio.

[0049] The electrode of a positive electrode and a negative electrode was obtained by carrying out the obtained slurry with ** on aluminum foil by the doctor blade method, and removing a N-methyl-2-pyrrolidone. Roll pressurization was carried out in order to raise further the **** filling factor of the obtained electrode active material, the electrode sheet obtained further was cut out in 25mmx25mm size, and the electrode was obtained. The thickness of the obtained electrode was 70 micrometers respectively.

[0050] The N-methyl-2-pyrrolidone in which the polyvinylidene fluoride was dissolved was distributed like the electrode, and the solid electrolyte adjusted the slurry. At this time, the mixing ratio of a solid electrolyte and a polyvinylidene fluoride was set to 93:7 by the weight ratio.

[0051] The layered product of a positive-electrode-solid electrolyte was obtained by carrying out with ** on the positive electrode which was able to obtain the obtained slurry first, and removing a N-methyl-2-pyrrolidone. Furthermore, the negative electrode obtained previously at the solid electrolyte side of this layered product was piled up, and it pressurized at the temperature of 160 degrees C in order to raise adhesion. The pressurization load at this time was set to 80MPa(s). Moreover, the thickness of a solid electrolyte was 27 micrometers.

[0052] The lithium cell of a square shape was assembled like the example 1 using the obtained layered product.

[0053] The synthetic method of the [example 2 of comparison] positive active material and a negative-electrode active material performed formation of an electrode like the example 1 of comparison like the example. The electrode thickness at this time was 65 micrometers respectively.

[0054] The bulk object with a thickness [of a crystalline substance] of 50 micrometers which can be expressed with Li1+x+yAlxTi2-xSiyP3-yO12 was used for the solid electrolyte. This solid electrolyte bulk object was pinched by the electrode which was able to be obtained first, and the layered product of a positive-electrode-solid electrolyte-negative electrode was produced.

[0055] The lithium cell of a square shape was assembled like the example 1 using the obtained

layered product.

[0056] The square shape solid electrolyte cell obtained in this way is used. (Evaluation) With a charging and discharging device It charges to 1.5V with the current of 100microA/cm2,200microA/cm2,500microA/cm2 as charge conditions at the above-mentioned square shape solid electrolyte cell. After suspended charge, holding for 5 minutes, discharging with the current same to the voltage of after that 0.5V as the time of charge, charging to 1.5V again next, after voltage reached 1.5V, and reaching this voltage, charge-and-discharge cycle evaluation which suspends charge and is held for 5 minutes was performed.

[0057] The result is shown in Table 1. In addition, the number of front Naka shows the service capacity to each discharge current, and a unit is mAh.

[0058]

[Table 1]

	放電電流 [μA／cm²]		
	100	200	500
実施例1	18.5	17.8	17.1
実施例2	18.3	17.5	168
比較例1	6.6	4.3	—
比較例2	16.2	15.3	14.4

[0059] Moreover, flexible evaluation was performed using the layered product of the positive-electrode-solid electrolyte-negative electrode produced in the example 1, the example 2, the example 1 of comparison, and the example 2 of comparison. The evaluation method was twisted around the glass rod of the shape of a pillar with a diameter of 10mm, and checked the crack and crack of a layered product. Consequently, the crack and the crack were not checked other than example of comparison 2 which used the bulk object for the solid electrolyte.

[0060] While the charge-and-discharge property that the lithium cell of this invention is equivalent to the lithium cell which used the solid electrolyte bulk object is acquired from the above thing, it turns out that it excels also in flexibility. Even if especially the discharge current becomes large, it is remarkable that the fall of the discharge current is small.

[0061] By making the compound which makes siloxane combination the main skeleton intervene between a positive electrode and a negative-electrode active material, this enables junction of an electrode and a solid electrolyte and is considered because resistance of an interface was reduced further. Furthermore, it is thought that junction of electrode active material powder and junction of an electrode and a solid electrolyte are performed, a reaction with an electrode active material being unable to occur easily, and maintaining the property of electrode active material original, in order to form siloxane combination in the process of heat treatment, if this invention is approached. Moreover, since acrylic resin is combined with the compound which makes siloxane combination the main skeleton, it becomes possible to also have flexibility.

[0062]

[Effect of the Invention] As mentioned above, according to the solid electrolyte cell concerning this invention, junction of an electrode and a solid electrolyte becomes firm by making the compound which makes the main skeleton siloxane combination (Si-O) which acrylic resin combined intervene between the active material powder which constitutes an electrode, and solid electrolyte powder. It has, and the touch area of an interface can become large, can reduce the internal resistance of a cell, and can obtain the lithium cell excellent in the charge-and-discharge property.

[0063] Furthermore, since acrylic resin has combined with siloxane combination, it becomes possible to have flexibility and the lithium cell which is excellent in flexibility nature can be obtained.

[0064]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a lithium cell.

[Translation done.]

* NOTICES *

PRIOR ART

[Description of the Prior Art] The lithium ion battery is widely used as power supplies, such as a cellular phone and a notebook computer, taking advantage of the property which is high-energy density.

[0003] Although these lithium ion batteries have cylindrical and a square shape, all insert the electrode group by which the positive electrode and the negative electrode were ****(ed) through separator into a battery-case can, and they have structure which it obturated by pouring in the organic electrolytic solution. LiClO4, LiPF6, LiBF4, etc. are dissolved in this as lithium salt by using that this organic electrolytic solution has propylene carbonate (PC), dimethyl ethane (DME), diethyl carbonate (DME), independent ethylene carbonate (EC), etc. or the mixed thing as a solvent.

[0004] In recent years, with the thin shape of the various electronic application devices represented by portable information terminal equipments, such as video photography equipment, and a notebook computer, a cellular phone, and the demand of a lightweight miniaturization, it replaces with the above organic electrolytic solutions, and the polymer electrolyte cell which mixed and arranged a polyelectrolyte and the organic electrolytic solution in inter-electrode [of a positive/negative couple] attracts attention.

[0005] However, since these lithium ion batteries and a polymer battery contain the organic electrolytic solution, they may start problems, such as a liquid spill and emitting smoke.

[0006] In order to solve this problem, development of the lithium cell which used the solid electrolyte of an inorganic system for the electrolyte is performed briskly.

[0007] The lithium cell using the inorganic solid electrolyte of lithium ion conductivity which consists of the glass of a sulfide system is raised in the lithium cell using the solid electrolyte of such an inorganic system. This inorganic solid electrolyte has the lithium ion conductivity which is equal to the organic electrolytic solution. However, the glass of a sulfide system is rich in reactivity, and has the problem of being easy to react especially with moisture and air.

[0008] On the other hand, in the solid electrolyte of an oxide system, the solid electrolyte in which a sodium ion conductivity solid electrolyte (NASICON system material) and the lithium ion conductivity crystalline-substance solid electrolyte which has the same crystal structure have the lithium ion conductivity of 1x10-3 - 1x10-4 S-cm -1 in recent years is proposed.

[0009] For example, the thing made to sinter the granular electrolyte expressed with Li1+(4-n) xMxTi2-x(PO4)3 (2 n= when a univalent or divalent cation and M of M are univalent and n= 1 and M are divalent x 0.1-0.5) in JP,5-299101,A. The lithium ion conductivity of 1x10-3 - 1x10-4 S-cm -1 has been obtained.

[0010] Moreover, heat treatment after fusing and fabricating P2O5 of a predetermined composition ratio, SiO2, TiO2 and aluminum 2O3, Li2O, etc. in JP,10-97811,A. By depositing Li1+x+yAlxTi2-yP3-yO12 (0<=x<=0.4, 0< y<=0.6), the solid electrolyte which has the lithium ion conductivity of 1.0x10-3 - 2.0x10-3 S-cm -1 is proposed.

[0011] Moreover, in JP,6-111831,A, the positive electrode which consists of a multiple oxide of MnO2 or alkali metal, and manganese, and a solid electrolyte are solid electrolytes which it really comes to form. When a solid electrolyte makes a lithium compound react to the multiple oxide of MnO2 or alkali metal, and manganese and forms three layer of Li2MnO(s) on the surface of a positive electrode, the touch area of the interface of a positive electrode and a solid electrolyte was enlarged, internal resistance of a cell was made small, and it has proposed raising a charge-and-

discharge property.

[0012] Moreover, the negative electrode which consists of the mixture of the positive electrode and negative-electrode active material powder which consist of the mixture of a solid electrolyte layer or positive-active-material powder, and solid electrolyte powder in JP,8-138724,A, and solid electrolyte powder. After pinching the solid electrolyte layer obtained by carrying out pressing of the solid electrolyte powder, it has proposed that the solid electrolyte layer to which it becomes field contact and grain-boundary resistance becomes small is obtained by pressurizing at the temperature below a glass transition point above the softening temperature of the aforementioned solid electrolyte.

[0013] Moreover, in JP,6-76828,A, in order to obtain the lithium ion conductivity solid electrolyte Plastic solid having high ion conductivity, and mechanical strength and high processability, the method of carrying out dry type kneading of a lithium ion conductivity sulfide solid electrolyte and the macromolecule elastic body is proposed.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, according to the solid electrolyte cell concerning this invention, junction of an electrode and a solid electrolyte becomes firm by making the compound which makes the main frame siloxane combination (Si-O) which acrylic resin combined intervene between the active material powder which constitutes an electrode, and solid electrolyte powder. It has, and the touch area of an interface can become large, can reduce the internal resistance of a cell, and can obtain the lithium cell excellent in the charge-and-discharge property.
[0063] Furthermore, since acrylic resin has combined with siloxane combination, it becomes possible to have flexibility and the lithium cell which is excellent in flexibility nature can be obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Conventionally, in the case of the cell using a solid electrolyte, it was formed in many cases only with the pressure welding, and the touch area of an electrode and a solid electrolyte was small, the bonding strength became weak, the resistance in these interfaces became large, the internal resistance as a cell became large, and junction of an electrode and a solid electrolyte had the fault that a charge-and-discharge property was inferior. The voltage drop resulting from the internal resistance of a cell became large, and there was a problem that current density was restricted as especially the charge and discharge current became large.

[0015] Moreover, since an ionic conduction path has many which have the anisotropy as for the solid electrolyte of a crystalline substance, the grain-boundary resistance in a solid electrolyte poses a problem. Therefore, the solid electrolyte of a crystalline substance serves as a proposal for which the lithium cell of JP,5-299101,A improves this problem, using a sintered compact in many cases. However, the problem of this ionic conduction path corresponds also about an electrode and a solid electrolyte interface, and the problem that resistance of an interface becomes large is left behind in contact only by the pressure welding.

[0016] Although the lithium cell of JP,6-111831,A is a proposal which improves the interfacial resistance of an electrode and a solid electrolyte, it has the problem that this method has complicated processes, such as forming MnO2 by sputtering or making above-mentioned MnO2 and above-mentioned LiOH formation of Li2MnO3 react etc.

[0017] Although pressing of the lithium cell of JP,8-138724,A is carried out at the temperature below a glass transition point above the softening temperature of a solid electrolyte, the grain boundary in a solid electrolyte is reduced in this case, and although the lithium ion conductivity as a solid electrolyte improves, in the process of heat-treatment, it forms a reaction layer in the interface of an electrode and a solid electrolyte, and has the problem that the reaction layer checks lithium ion conduction.

[0018] Furthermore, as above-mentioned, the lithium cell using these solid electrolytes carries out pressing of the inorganic powder, or performs pressurization and heating simultaneously and is formed. Therefore, the lithium cell obtained had the problem that it was hard and was weak. The lithium ion conductivity solid electrolyte Plastic solid having a mechanical strength and high processability is obtained by carrying out dry type kneading and fabricating a lithium ion conductivity sulfide solid electrolyte and a macromolecule elastic body with the lithium cell of JP,6-76828,A to this problem. However, since a sulfide noncrystalline-solid electrolyte reacted with a solvent and a hydrogen sulfide was produced when operation in air atmosphere is difficult and a protic solvent is used [in / the production process / since it is limited to a lithium ion conductivity solid electrolyte containing a sulfuration lithium in this case] for a solvent, there was a problem that mixture with a lithium ion conductivity solid electrolyte and a macromolecule elastic body had to be performed by dry type kneading.

[0019] It is made in view of the above conventional troubles, and the bonding strength of an electrode and a solid electrolyte is weak, the internal resistance as a cell becomes large, and this invention aims to let it give flexibility to a lithium cell to offer the solid electrolyte cell which canceled the conventional trouble that a charge-and-discharge property was inferior.

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned problem, in the lithium cell concerning a claim 1, it is characterized by the compound which makes the main skeleton siloxane combination (Si-O) which acrylic resin combined between the aforementioned active material powder and solid electrolyte powder intervening in the lithium cell which arranged the solid electrolyte in inter-electrode [of the positive/negative couple which consists mainly of an active material].
[0021] The thing which is chosen as the compound which makes the main skeleton siloxane combination which the aforementioned acrylic resin combined in the above-mentioned lithium cell from In 2O3 which doped SnO2 or SnO2 which doped RuO2 or Sb 2O3 and which add more than a kind at least is desirable.
[0022] It is desirable for the carbon material to have combined with the compound which makes the main skeleton siloxane combination which the aforementioned acrylic resin combined in the above-mentioned lithium cell.
[0023]
[Embodiments of the Invention] Hereafter, the operation gestalt of the lithium cell concerning a claim 1 is explained. Drawing 1 is the cross section showing the example of composition of the lithium cell concerning a claim 1. drawing 1 -- setting -- 1 -- for a positive electrode and 2b, as for a solid electrolyte layer and 4, a negative electrode and 3 are [a package and 2 / the electrode of a couple, and 2a / a positive-electrode charge collector and 5] negative-electrode charge collectors
[0024] If airtightness can be held, a package 1 is not limited to the quality of the material, for example, can use metals, such as lamination material made from aluminum, nickel, and aluminum, or a shrink case.
[0025] The positive-electrode charge collector 4 or the negative-electrode charge collector 5 is formed for current collection of positive-electrode 2a or negative-electrode 2b, for example, metallic foils, such as aluminum (aluminum), nickel (nickel), and copper (Cu), can be used for it.
[0026] As for the active material of an electrode 2 (2a, 2b), for example, a lithium manganese multiple oxide, manganese dioxide, a lithium nickel multiple oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, a niobium oxide, a vanadium oxide, tungstic oxides, etc. and those ****** are mentioned. Furthermore, in the lithium cell using the solid electrolyte 3, in order to use neither separator nor the organic electrolytic solution, there is a limit which permits expansion contraction of the electrode accompanying charge and discharge. Therefore, especially as an active material used for an electrode 2 (2a, 2b), it is desirable to choose either Li1+xMn2-xO4 (0<=x<=0.2), LiMn2-yMeyO4 (Me=nickel, Zn [Cr, Cu and Zn], 0< y<=0.6), Li4Ti 5O12 or Li4Mn 5O12. Here, what shows **** potential to a positive electrode for what a clear distinction does not have in a positive active material and a negative-electrode active material, compares the charge and discharge potential of two kinds of compounds, and shows electropositive potential can be used for a negative electrode, respectively, and the cell of arbitrary voltage can be constituted.
[0027] The compound which makes the main skeleton siloxane combination (Si-O) which acrylic resin combined is made to intervene between this active material powder. A silane compound is raised as a compound which forms siloxane combination. With a silane compound, a tetramethoxy silane, methyl trimetoxysilane, dimethyl dimethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, a tetrapod ethoxy silane, methyl triethoxysilane, dimethyl diethoxysilane, phenyl

triethoxysilane, diphenyl diethoxysilane, hexyl trimethoxysilane, the poly methoxy siloxane, a poly ethoxy siloxane, a poly butoxy siloxane, etc. are mentioned. As a method of combining these silanes compound and acrylic resin, the cold blend of acrylic and the silane system is carried out, and the method of making it understand an added water part is mentioned. Moreover, solvents, such as a methanol, ethanol, or isopropyl alcohol, can be mixed if needed, and these solvents can also be evaporated simultaneously with hydrolysis. Considering unity with acrylic resin, as a silane compound, the poly methoxy siloxane, a poly ethoxy siloxane, and a poly butoxy siloxane are desirable.

[0028] Junction of an electrode 2 and a solid electrolyte 3 is based neither on sticking by pressure nor a reaction layer, and is formed with the compound which makes the main skeleton siloxane combination which the acrylic resin made to intervene between active material powder combined. Siloxane combination which this acrylic resin combined forms combination of active material powder, solid electrolyte powder and an electrode, and a solid electrolyte at the same time it is formed by heat treatment. When forming siloxane combination which acrylic resin combined, the compound which makes the main skeleton siloxane combination which temperature did not need to be raised too much, and could suppress the reaction of an electrode 2 and a solid electrolyte 3, and acrylic resin combined can also suppress a reaction with an electrode active material.

[0029] Moreover, lithium ion conductivity glass ceramics can form a firm combination, and the compound which makes the main skeleton siloxane combination which the acrylic resin which intervenes between electrode active materials combined can strengthen junction of an electrode 2 and a solid electrolyte 3 for them. Therefore, the touch area of an interface can reduce the internal resistance of a cell by the bird clapper greatly.

[0030] As a solid electrolyte 3, it divides roughly and is classified into a sulfide system and an oxide system. In the solid electrolyte of a sulfide system, although the lithium ion conductivity in a room temperature has the property which is equal to 1x10-3 S-cm -1 and the organic electrolytic solution, it has problems, such as being hygroscopic. Therefore, it is more desirable to use an oxide system for a solid electrolyte 3. In it, lithium ion conductivity is about -one 1x10-6 S-cm at a room temperature, and it is difficult for the solid electrolyte of an amorphous system to fully fulfill a property. The lithium ion conductivity of the solid electrolyte of a crystalline substance is about -one 1x10-3 S-cm - 1 - 1x10-4 S-cm at a room temperature to it. Therefore, as for the solid electrolyte 3 to be used, it is more desirable that it is the solid electrolyte of a crystalline substance. It is desirable that it is the solid electrolyte of the crystalline substance which has the lithium ion conductivity which contains a lithium (Li), titanium (Ti), and a Lynn (P) and oxygen (O) element especially. Li1+xMxTi2-x(PO4)3 (here -- M -- aluminum, Sc, and Y --) La), Li1+xTi2-x(PO4)3, Li0.5-3xR0.5+xTiO3 (it La(s) R here) Pr, Nd, Sm, Li1+x+yMxTi2-xSiyP3-yO12 (M is aluminum, Ga, 0<=x<=0.4, and 0< y<=0.6 here), Li1+(4-n) MxTi2-x(PO4)3 (M is a univalent or divalent cation), etc. are mentioned.

[0031] An electronic-conduction assistant is added by the electrode 2 (2a, 2b) if needed. As an electronic-conduction assistant, SnO2, In 2O3, TiO2-x, ZnO and Fe 3O4, ReO3, MoO2, RuO2 and VO, and WO2 grade are mentioned as an oxide, for example. In order to obtain the stable low resistivity, the thing which is chosen from In 2O3 which doped SnO2 or SnO2 which doped RuO2 or Sb 2O3 and which contain more than a kind at least is desirable. Moreover, when using an oxide, as for the addition as an electronic-conduction assistant, it is desirable that it is 10 - 50wt% to an active material. When there are few electronic-conduction assistants than these additions, grant of electronic-conduction nature is not enough, and when [than these additions] more, although an electronic conduction is securable, an electronic-conduction assistant may intervene between electrode active materials, may check conduction of a lithium ion, and is not desirable [an electronic conduction].

[0032] Moreover, when the carbon material has combined with the compound which makes the main skeleton siloxane combination which acrylic resin combined, addition of the above-mentioned electronic-conduction assistant is not needed, but the carbon material combined with the compound which makes the main skeleton siloxane combination which acrylic resin combined serves as an electronic-conduction assistant. As a carbon material, acetylene black, carbon black, KETCHIEN black, etc. are mentioned. Moreover, a carbon material is combined by replacing by OR machines

(R : a methyl group, an ethyl group, etc.) of the silane compound which acrylic resin combined.

[0033] The following methods are mentioned as the production method of an electrode 2 (2a, 2b) and a solid electrolyte 3. The silane compound which mixed electronic-conduction assistant powder beforehand and acrylic resin combined with a positive electrode, negative-electrode active material powder, and solid electrolyte powder when required is distributed. Slurry viscosity is adjusted while adding and slurring solvents, such as isopropyl alcohol, if needed. At this time, mixture of electronic-conduction assistant powder is unnecessary to solid electrolyte powder.

[0034] Moreover, in order to stiffen the silane compound which acrylic resin combined, the catalyst for hardening can also be used. Before distributing powder, even if it adds, after distributing powder, you may add this catalyst for hardening.

[0035] By the doctor blade method or the roll-coater method, after applying the slurry obtained in this way on the positive-electrode charge collector 4 or the negative-electrode charge collector 5, it stiffens the silane compound which combined acrylic resin. When the catalyst for hardening is used for hardening conditions, although the holding time becomes short so that about 150 degrees C is suitable from ordinary temperature and a curing temperature is high, a curing temperature and especially time are not restricted. Moreover, when not using the catalyst for hardening, it is desirable to heat at the temperature of 150 degrees C or more, and maximum temperature is about 300 degrees C from which acrylic resin starts a decomposition reaction.

[0036] You may make an electrode 2 mix the solid electrolyte which is the same composition as a solid electrolyte 3 here if needed.

[0037] Moreover, the method of stiffening, after having fabricated the method of carrying out heat hardening by package after carrying out the laminating of positive-electrode 2a, negative-electrode 2b, and the laminating method of a solid electrolyte 3 to the order of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b, positive-electrode 2a, and negative-electrode 2b after carrying out heat hardening, fabrication and, fabricating a solid electrolyte 3 on one of electrodes separately and piling up another electrode etc. is mentioned. Furthermore, if it pressurizes at the time of heat hardening, while the filling factor of **** will improve, since junction of the electrode 2-solid electrolyte 3 becomes firmer, it is desirable.

[0038] Even if the solid electrolyte cell to which this invention is applied is a primary cell, it may be a rechargeable battery. A cell configuration is not limited to cylindrical, a square shape, a button type, a coin type, a flat type, etc.

[Translation done.]

* NOTICES *

EXAMPLE

[Example] A [example 1] lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 1.1:1.9, by carrying out heating baking of this mixture at 650 degrees C in the atmosphere for 15 hours, the lithium manganese multiple oxide (Li1.1Mn 1.9O4) was compounded, and this was made into the positive active material. Next, a lithium hydroxide and manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 4:5, the lithium manganese multiple oxide (Li4Mn 5O12) was compounded by carrying out heating baking of this mixture at 600 degrees C in the atmosphere for 15 hours, and this was made into the negative-electrode active material.

[0040] The siloxane compound which acrylic resin combined was prepared in the following procedures. To the siloxane compound (siloxane compound concentration : about 30 wt(s)% and acrylic resin concentration : about 20 wt(s)%, a solvent : about 50 wt(s)%) which acrylic resin combined, the catalyst for hardening of a maleic-acid system was mixed, it stirred in ordinary temperature, and mixed liquor was produced. At this time, the mixing ratio of the catalyst for hardening was set to 3g to 100g of siloxane compounds which acrylic resin combined. Moreover, in order to attain stabilization of mixed liquor, it put in ordinary temperature for 12 hours. (Let this be adjustment mixed liquor below.)

Adjustment mixed liquor was made to distribute an above-mentioned positive electrode and an above-mentioned negative-electrode active material with RuO2 which is an electronic-conduction assistant, respectively, and the slurry was produced. The mixing ratio of the active material powder at this time, RuO2, and adjustment mixed liquor was set to 2:1:1 by the weight ratio. Subsequently, after fabricating this slurry by the doctor blade method on aluminum foil, heat hardening was carried out on 150-degree-C conditions for 30 minutes. Furthermore, this was judged in 25mmx25mm size, and positive-electrode 2a negative-electrode 2b was obtained. Positive-electrode 2a and negative-electrode 2b of the thickness at this time were 75 micrometers.

[0041] As a solid electrolyte 3, the main crystal phase used the solid electrolyte of the crystalline substance which can be expressed with Li1+x+yAlxTi2-xSiyP3-yO12. Adjustment mixed liquor was made to distribute a powdered solid electrolyte, and the slurry was produced. This slurry was fabricated by the doctor blade method on the above-mentioned positive-electrode 2a, it piled up on the solid electrolyte 3 which subsequently applied negative-electrode 2b, heat hardening was carried out on 150-degree-C conditions for 30 minutes, and the layered product of positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was produced. The thickness of the solid electrolyte 3 at this time was 30 micrometers.

[0042] The lamination made from aluminum of a package 1 was equipped with the obtained layered product. The lamination made from aluminum prepared two things cut in 35mmx35mm size, is carrying out thermocompression bonding of the periphery section of the lamination made from aluminum on both sides of the layered product which joined the charge collector, and assembled the 35mmx35mm square shape lithium cell shown in drawing 1 .

[0043] The synthetic method of a [example 2] positive active material and a negative-electrode active material was performed like the example 1.

[0044] What the carbon material combined (siloxane compound concentration : about 25 wt(s)% and acrylic resin concentration : about 15 wt(s)% and acetylene black concentration : about 10 wt(s)%, a solvent : about 50 wt(s)%) was used for the siloxane compound which acrylic resin combined.

[0045] Hereafter, the production method of production of adjustment mixed liquor and positive-electrode 2a-solid electrolyte 3-negative-electrode 2b was performed like the example 1. The thickness of the electrode obtained here was 70 micrometers, and the thickness of a solid electrolyte was 35 micrometers.

[0046] The production method of a square shape lithium cell was performed like the example 1.

[0047] The synthetic method of the [example 1 of comparison] positive active material and a negative-electrode active material was performed like the example 1.

[0048] The following procedures performed formation of an electrode. The N-methyl-2-pyrrolidone in which the polyvinylidene fluoride was dissolved was made to distribute respectively the positive electrode and negative-electrode active material which were obtained previously, and carbon black, and the slurry was adjusted. At this time, the mixing ratio of an electrode active material, carbon black, and a polyvinylidene fluoride was set to 85:12:7 by the weight ratio.

[0049] The electrode of a positive electrode and a negative electrode was obtained by carrying out the obtained slurry with ** on aluminum foil by the doctor blade method, and removing a N-methyl-2-pyrrolidone. Roll pressurization was carried out in order to raise further the **** filling factor of the obtained electrode active material, the electrode sheet obtained further was cut out in 25mmx25mm size, and the electrode was obtained. The thickness of the obtained electrode was 70 micrometers respectively.

[0050] The N-methyl-2-pyrrolidone in which the polyvinylidene fluoride was dissolved was distributed like the electrode, and the solid electrolyte adjusted the slurry. At this time, the mixing ratio of a solid electrolyte and a polyvinylidene fluoride was set to 93:7 by the weight ratio.

[0051] The layered product of a positive-electrode-solid electrolyte was obtained by carrying out with ** on the positive electrode which was able to obtain the obtained slurry first, and removing a N-methyl-2-pyrrolidone. Furthermore, the negative electrode obtained previously at the solid electrolyte side of this layered product was piled up, and it pressurized at the temperature of 160 degrees C in order to raise adhesion. The pressurization load at this time was set to 80MPa(s). Moreover, the thickness of a solid electrolyte was 27 micrometers.

[0052] The lithium cell of a square shape was assembled like the example 1 using the obtained layered product.

[0053] The synthetic method of the [example 2 of comparison] positive active material and a negative-electrode active material performed formation of an electrode like the example 1 of comparison like the example. The electrode thickness at this time was 65 micrometers respectively.

[0054] The bulk object with a thickness [of a crystalline substance] of 50 micrometers which can be expressed with Li1+x+yAlxTi2-xSiyP3-yO12 was used for the solid electrolyte. This solid electrolyte bulk object was pinched by the electrode which was able to be obtained first, and the layered product of a positive-electrode-solid electrolyte-negative electrode was produced.

[0055] The lithium cell of a square shape was assembled like the example 1 using the obtained layered product.

[0056] The square shape solid electrolyte cell obtained in this way is used. (Evaluation) With a charging and discharging device It charges to 1.5V with the current of 100microA/cm2,200microA/cm2,500microA/cm2 as charge conditions at the above-mentioned square shape solid electrolyte cell. After suspended charge, holding for 5 minutes, discharging with the current same to the voltage of after that 0.5V as the time of charge, charging to 1.5V again next, after voltage reached 1.5V, and reaching this voltage, charge-and-discharge cycle evaluation which suspends charge and is held for 5 minutes was performed.

[0057] The result is shown in Table 1. In addition, the number of front Naka shows the service capacity to each discharge current, and a unit is mAh.

[0058]

[Table 1]

	放電電流 [μA／cm²]		
	100	200	500
実施例1	18.5	17.8	17.1
実施例2	18.3	17.5	168
比較例1	6.6	4.3	—
比較例2	16.2	15.3	14.4

[0059] Moreover, flexible evaluation was performed using the layered product of the positive-electrode-solid electrolyte-negative electrode produced in the example 1, the example 2, the example 1 of comparison, and the example 2 of comparison. The evaluation method was twisted around the glass rod of the shape of a pillar with a diameter of 10mm, and checked the crack and crack of a layered product. Consequently, the crack and the crack were not checked other than example of comparison 2 which used the bulk object for the solid electrolyte.

[0060] While the charge-and-discharge property that the lithium cell of this invention is equivalent to the lithium cell which used the solid electrolyte bulk object is acquired from the above thing, it turns out that it excels also in flexibility. Even if especially the discharge current becomes large, it is remarkable that the fall of the discharge current is small.

[0061] By making the compound which makes siloxane combination the main frame intervene between a positive electrode and a negative-electrode active material, this enables junction of an electrode and a solid electrolyte and is considered because resistance of an interface was reduced further. Furthermore, it is thought that junction of electrode active material powder and junction of an electrode and a solid electrolyte are performed, a reaction with an electrode active material being unable to occur easily, and maintaining the property of electrode active material original, in order to form siloxane combination in the process of heat treatment, if this invention is approached. Moreover, since acrylic resin is combined with the compound which makes siloxane combination the main frame, it becomes possible to also have flexibility.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the cross section showing 1 operation gestalt of the lithium cell concerning this invention.
[Description of Notations]
1: A package, the electrode of 2:couple, a 2a:positive electrode, a 2b:negative electrode, 3:solid electrolyte layer, 4:positive-electrode charge collector, 5 : negative-electrode charge collector

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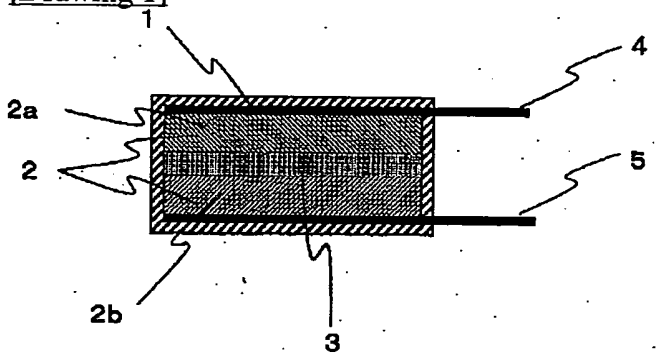
DRAWINGS

[Drawing 1]



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